Nanocomposite Edible Films from Mango Puree Reinforced with Cellulose Nanofibers

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ABSTRACT: Cellulose nanoreinforcements have been used to improve mechanical and barrier properties of biopolymers, whose performance is usually poor when compared to those of synthetic polymers. Nanocomposite edible films have been developed by adding cellulose nanofibers (CNF) in different concentrations (up to 36 g/100 g) as nanoreinforcement to mango puree based edible films. The effect of CNF was studied in terms of tensile properties, water vapor permeability, and glass transition temperature (T_g) of the nanocomposite films. CNF were effective in increasing tensile strength, and its effect on Young's modulus was even more noticeable, especially at higher concentrations, suggesting the formation of a fibrillar network within the matrix. The addition of CNF was also effective to improve water vapor barrier of the films. Its influence on T_g was small but significant. The study demonstrated that the properties of mango puree edible films can be significantly improved through CNF reinforcement.

Keywords: edible film, food packaging, mechanical properties, nanofibers, nanotechnology

Introduction

Food and beverage packaging is responsible for about 70% of the packaging market in the United States, and more than half the worldwide market (Stevens 2002). This large volume of food packaging is meant to be quickly discarded, and the waste volume has not been greatly reduced by the recycling programs, because of high recycling costs and difficulties related to polymer separation (Azapagic and others 2003).

Several edible materials have had their film-forming properties studied, to produce edible films to be used in food packaging, not to completely replace synthetic plastics, but rather to improve their efficiency, thus reducing the amount of synthetic polymers required for each application. Fruit and vegetable purees and concentrates have been recently studied as film-forming edible materials (McHugh and others 1996; McHugh and Senesi 2000; Senesi and McHugh 2002; Rojas-Graü and others 2006, 2007). Such application of fruit and vegetable purees is related to the presence of polysaccharides in their composition, such as pectin, starch, and cellulose derivatives (Kaya and Maskan 2003). Edible films produced from fruit purees can combine the mechanical and barrier properties from the film-forming components with the color and flavor provided by the pigments and volatile compounds of the fruit. Moreover, the production of edible films is an interesting and promising way of using coproducts of fruit processing.

The commercial use of edible films has been limited because of problems related to their usually poor mechanical and barrier properties when compared to synthetic polymers. Several composites have been developed by adding reinforcing compounds (fillers) to polymers to enhance their thermal, mechanical, and barrier properties. However, many reinforced materials present poor adhesion at the interface of their components. Macroscopic reinforcing components often contain defects, which become less important as the particles of the reinforcing component are smaller (Ludueña and others 2007). The application of nanotechnology to edible polymers may open new possibilities for improving not only the properties but also the cost-price efficiency (Sorrentino and others 2007). The use of fillers that have at least 1 dimension in the nanometric range (nanoparticles) produces polymer nanocomposites (Alexandre and Dubois 2000). A uniform dispersion of nanoparticles leads to a very large matrix/filler interfacial area, which changes the molecular mobility, the relaxation behavior, and the consequent thermal and mechanical properties of the material. High aspect ratio fillers are particularly interesting because of their high specific surface area, providing better reinforcing effects (Azizi Samir and others 2005; Dalmas and others 2007).

Cellulose is a highly strong natural polymer. Cellulose nanofibers are an attractive class of nanomaterials for elaboration of low cost, lightweight, and high-strength nanocomposites (Helbert and others 1996; Podsiadlo and others 2005). In plants or animals, the cellulose chains are synthesized to form nanofibers, which are bundles of molecules that are elongated and stabilized through hydrogen bonding (Azizi Samir and others 2005; Wang and Sain 2007). Nanofibers are nanosized in diameters (2 to 20 nm, depending on the origin), and lengths ranging from a few hundred up to thousands of nanometers (Azizi Samir and others 2005; Oksman and others 2006).

This study was the first to evaluate the effect of different concentrations of cellulose nanofibers added as a nanoreinforcing component on tensile properties, water vapor permeability and glass transition temperature of mango puree edible films.

Materials and Methods

Mango-puree solution formulation and film casting

The mango puree (29% total solids, 27.5% soluble solids) was obtained from Keitt mangoes. The cellulose nanofibers (CNF,

Novacel® PH-101) were provided by FMC BioPolymer (Philadelphia, Pa., U.S.A.).

An aliquot of the CNF suspension was mixed with an equal volume of 2% uranyl acetate (UA). A 10 μL drop of the UA-fibril mixture was dispensed onto a 400-mesh copper grid, allowed to stand for 30 to 60 s, and the excess fluid was wicked off with Whatman nr 1 filter paper. The grid was air dried and viewed in a CM12 scanning-transmission electron microscope (STEM) (FEI Co. Inc., Hillsboro, Oreg., U.S.A.) operating in the bright field mode at 80 kV. Digital images were captured with the STEM's associated XR41 CCD camera system (AMT, Danvers, Mass., U.S.A.). Fiber lengths and widths were measured directly from transmission electron micrographs using Image Pro Plus 6.3 (Media Cybernetics Inc., Bethesda, Md., U.S.A.). Data were collected and analyzed using Microsoft Excel 2003 (Microsoft, Redmond, Wash., U.S.A.).

Different concentrations of CNF (ranging from 1 to 36 g per 100 g of mango puree, on a dry basis) were added to the mango puree, and the dispersions were homogenized at 6500 rpm for 30 min, using a Polytron PT 3000 (Brinkmann Instruments, Westbury, N.Y., U.S.A.). A control film was elaborated only with mango puree. The film-forming dispersions were submitted to vacuum to remove bubbles, and films were cast on leveled 29 × 29 cm square plates (45 g per plate) and allowed to dry for 16 h at 22 °C and 42% RH. Samples of the dried films were cut and peeled from the casting surface, and stored under refrigeration until analyses.

Analyses on mango puree edible films

Film thicknesses were measured with a micrometer IP 65 (Mitutoyo Manufacturing, Tokyo, Japan) to the nearest 0.001 mm, at 7 to 8 random positions around the film for samples designed for water vapor permeability (WVP) and tensile tests.

Tensile properties (tensile strength [TS], elongation at break [EB], and Young's modulus [YM]) were measured according to standard method D882-97 (ASTM 1997), using an Instron Model 55R4502 Universal Testing Machine (Instron, Canton, Mass., U.S.A.) with a 100 N load cell. The gravimetric modified cup method (McHugh and others 1993) based on standard method E96-80 (ASTM 1989) was used to determine WVP. The detailed methods for both WVP and tensile tests were described by Rojas-Graü and others (2007).

The glass transition temperature (T_g) of the nanocomposite films was measured by differential scanning calorimetry (DSC) using an mDSC 2910 (TA Instruments, New Castle, Del., U.S.A.). The DSC profiles were run from −40 to 40 °C, at a heating rate of 10 °C/min.

Eight specimens of mango puree edible film from each treatment were evaluated for measuring tensile properties and water vapor permeability. For T_g measurements, 4 specimens were evaluated.

The effect of CNF on physical properties was evaluated by comparing means of the properties of the films with different CNF concentrations by Tukey tests ($P < 0.05$).

The samples were prepared for scanning electron microscopy by dropping a 1 cm² piece cut from the center of the film into liquid nitrogen and allowing the piece to equilibrate under the liquid nitrogen. The film piece was then fractured into several smaller pieces with a prechilled razor blade held in a vice grip. The smaller pieces were removed and placed immediately on filter paper and transferred to a desiccator for 30 to 60 min. Selected smaller pieces were mounted individually edge-up on a small half stub which was in turn mounted to a full stub using double adhesive coated carbon tabs (Ted Pella, Inc, Redding, Calif., U.S.A.). The film samples were coated for 2 min with gold-palladium in a Denton Desk II sputter coating unit (Denton Vacuum, LLC, Moorestown, N.J., U.S.A.), and viewed and photographed in a Hitachi S4700 field emission scanning electron microscope (Hitachi, Tokyo, Japan).

Results and Discussion

Cellulose nanofibers are presented in Figure 1. Their average dimensions were: length, (82.6 ± 4.3) nm, and diameter, (7.2 ± 0.3) nm. Their aspect ratio (calculated by dividing fiber length by its diameter) was thus about 11.5. Their average diameter is within the range mentioned by other authors (8 to 10 nm, according to Lima and Borsali [2004]; less than 10 nm, according to Mathew and Dufresne [2002]). The average fiber length has been below the range reported in other studies (500 to 2000 nm, according to Mathew and Dufresne [2002]; 100 to 300 nm, according to Lima and Borsali [2004]), resulting in lower aspect ratios. Still, the average aspect ratio of the fibers has been higher than 10, considered as the minimum value for a good stress transfer from the matrix to the fibers for any significant reinforcement to occur (Jiang and others 2007; Mutjé and others 2007).

Figure 2 presents the ultrastructure of films produced from pure mango puree (control) and from puree with a CNF loading of 36 g/100 g (36 g of CNF per 100 g of mango puree). The nanofibers (appearing as lighter regions in Figure 2B) seem to have presented good interactions with the mango puree (darker regions). They were well dispersed in the matrix, without significant agglomeration. Interactions may have occurred between cellulose and neutral sugar side chains of mango pectin, as suggested in previous studies (Oechslin and others 2003; Vignon and others 2004; Zykwinska and others 2005). Zykwinska and others (2005) mentioned that, although there is little information about how pectin interacts with cellulose, it is likely that such interactions are mediated by hydrogen bonds. Moreover, the hydrophilic sites of mango starch may have also interacted with hydroxyl groups of cellulose (Averous and others 2001; Wu and others 2009) by hydrogen bonds (Chen and others 2009).

Table 1 presents physical properties of mango puree films containing different CNF concentrations. CNF were effective in
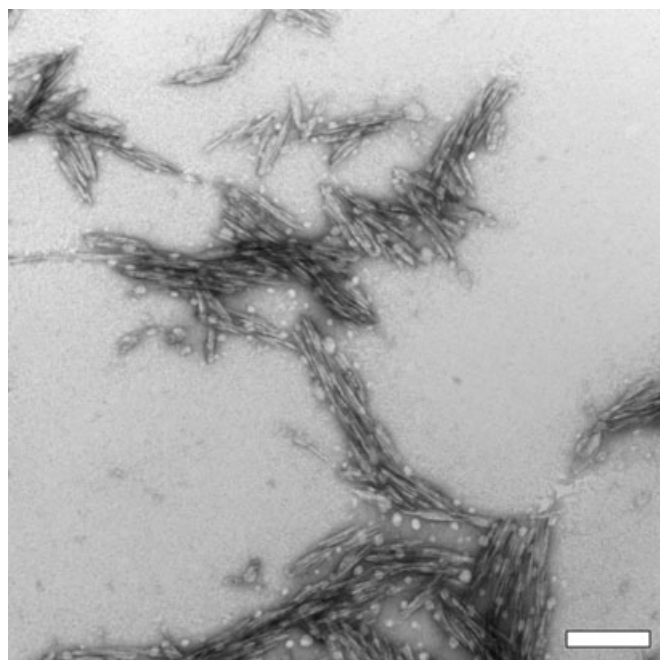

Figure 1 — Cellulose nanofibers visualized by TEM. Scale bar = 200 nm.

increasing tensile strength (at concentrations of 2 g/100 g or more) and Young's modulus (at concentrations ≥ 5 g/100 g). The elongation at break was not significantly impaired at CNF concentrations up to 10 g/100 g, while films with higher CNF concentrations presented decreased elongation when compared to the control. Figure 3 presents typical stress-strain curves obtained from mango puree edible films without CNF (control) and with CNF loadings of 10 g/100 g and 36 g/100 g (CNF10 and CNF36, respectively). Addition of CNF changed the stress-strain behavior showing mixed deformation mechanisms. The films CNF10 and CNF36 show yield stress at 3% elongation. Below this yield, those films followed a reversible elastic deformation with sharply increased elastic modulus compared with that of control film. Addition of CNF increased the elastic modulus of the films. At more than 3% elongation, those films were deformed irreversibly showing plasticity behaviors, while control film did not show any yield as indicated with a simple straight slope. After yield, the slopes of CNF10 and CNF36 did not show a significant difference. Also, when a 3% tensile deformation is reached, all cross-linkings made by CNF are already destroyed, and after the fracture of the nanofibers, CNF10 and CNF36 films show the same deformation mechanisms, which mainly happened at the amorphous area by the stretching and sliding of polymer molecules. Both tensile strength and elastic modulus of the nanocomposites were improved when compared to those of the neat mango puree matrix, corroborating several previous findings (Ljungberg and others 2005; Lu and others 2005; Dogan and McHugh 2007; Wang and Sain 2007; Tang and Liu 2008; Kim and others 2009). On the other hand, the effect of CNF on elongation depended on the loading of CNF. A loading of 10 g/100 g did not affect elongation, but when the loading was increased to 36 g/100 g, the elongation was impaired. Such a decreased elongation with high loading of CNF suggests a poor interaction between nanofibers and the mango puree matrix, as suggested by Kim and Jo (2009), although the good dispersion of the nanofibers (Figure 2) indicates a good interaction between the film components even with a CNF loading of 36 g/100 g. Zimmermann and others (2004) observed that, although a sharp rise has occurred in elongation with a loading of up to 5 g/100 g of nanofibers, higher loadings (10 to 20 g/100 g) resulted in decreased elongation. Other researchers also reported decreased elongation with addition of
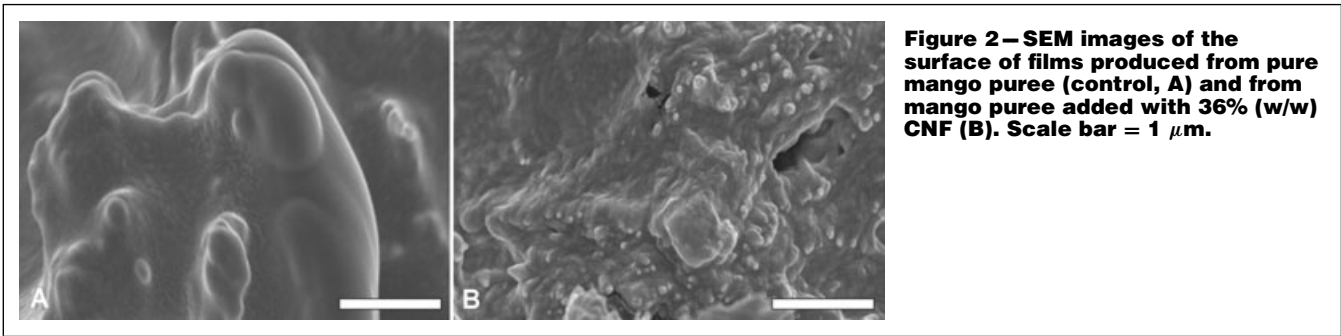

Figure 2—SEM images of the surface of films produced from pure mango puree (control, A) and from mango puree added with 36% (w/w) CNF (B). Scale bar = 1 μm.

Table 1—Physical properties of mango puree edible films with different concentrations of CNF nanoreinforcements.

CNF (g/100g)[A]	TS (MPa)	EB (%)	YM (MPa)	WVP (g.mm/kPa.h.m²)	T_g (°C)
0	(4.09 ± 0.12)[e]	(44.07 ± 0.98)[a]	(19.85 ± 0.51)[e]	(2.66 ± 0.06)[a]	(−10.63 ± 0.47)[e]
1	(4.24 ± 0.25)[de]	(42.42 ± 1.90)[ab]	(21.55 ± 0.98)[e]	(2.40 ± 0.19)[ab]	(−8.51 ± 0.46)[d]
2	(4.42 ± 0.14)[de]	(43.30 ± 1.46)[ab]	(22.56 ± 0.88)[e]	(2.17 ± 0.08)[bc]	(−8.57 ± 0.33)[d]
5	(4.58 ± 0.21)[cd]	(41.79 ± 0.44)[b]	(30.93 ± 1.27)[d]	(2.16 ± 0.05)[bc]	(−7.72 ± 0.26)[c]
10	(4.91 ± 0.13)[c]	(43.19 ± 1.73)[ab]	(40.88 ± 1.41)[c]	(2.03 ± 0.11)[c]	(−6.81 ± 0.36)[b]
18	(5.54 ± 0.07)[b]	(39.8 ± 0.53)[b]	(78.82 ± 5.00)[b]	(1.90 ± 0.06)[cd]	(−5.88 ± 0.25)[a]
36	(8.76 ± 0.11)[a]	(31.54 ± 2.29)[c]	(322.05 ± 19.43)[a]	(1.67 ± 0.11)[d]	(−6.04 ± 0.17)[a]

[A]Mass of CNF added to 100 g of mango puree, on a dry basis. TS = tensile strength (MPa); EB = elongation at break (%); YM = Young's modulus (MPa); WVP = water vapor permeability (g.mm/kPa.h.m²); T_g = glass transition temperature (°C). Means in same column with different letters are significantly different at $P < 0.05$.
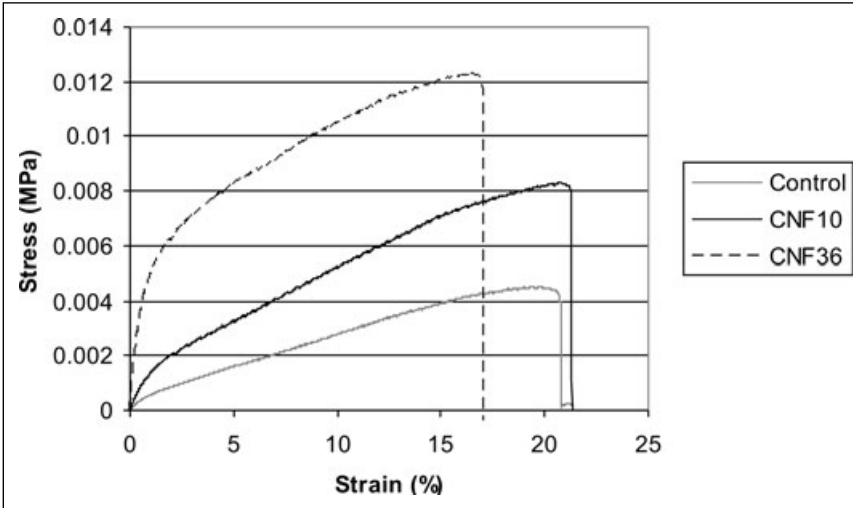

Figure 3—Typical stress-strain curves from mango puree edible films without CNF (control) and with CNF loadings of 10 g/100 g (CNF10) and 36 g7/100 g (CNF36).

cellulose nanofibers (Azizi Samir and others 2004; Ljungberg and others 2006; Leitner and others 2007; Roohani and others 2008; Tang and Liu 2008). In this study, the property most affected by CNF concentration was the modulus, which increased more than 100% when with a CNF loading of 10 g/100 g, and more than 1500% with a loading of 36 g/100 g. Other researchers (Helbert and others 1996; Wu and others 2007) observed similarly high (or even higher) influence of CNF on modulus of polymeric films. According to Helbert and others (1996), such a great effect is ascribed to the formation of a fibrillar network within the polymer matrix, the cellulose fibers being probably linked through hydrogen bonds. Zimmermann and others (2004) observed that nanofiber contents of up to 5 g/100 g resulted in no strength or stiffness improvement of poly(vinyl alcohol) composites, and they suggested that probably a minimum nanofiber content is required to induce intense interactions between nanofibers and thus the formation of networks.

WVP of the control film was comparable to the value (2.23 g.mm/kPa.h.m^2) reported by Hoagland and Parris (1996) for pectin films plasticized with lactic acid, suggesting that the polysaccharide content of the mango puree was high enough to produce a film with a fairly good water vapor barrier. The addition of at least 10 g of CNF per 100 g of matrix was effective to decrease WVP of mango puree films, similar to results reported by Paralikar and others (2008) and Sanchez-Garcia and others (2008), by addition of cellulose nanofibers to other polymeric films. Different results were reported by Dogan and McHugh (2007), who have observed no significant changes in WVP of hydroxyl propyl methyl cellulose (HPMC) films by CNF addition (in loadings up to 25 g/100 g). The presence of crystalline fibers is thought to increase the tortuosity in the materials leading to slower diffusion processes and, hence, to lower permeability (Sanchez-Garcia and others 2008). The barrier properties are enhanced if the filler is less permeable, and have good dispersion in the matrix and a high aspect ratio (Lagaron and others 2004). In the present study, the interactions of CNF with mango components (mainly pectin and/or starch) as well as the interactions between nanofibers may have favored the water vapor barrier.

Since the soluble solid content of the mango puree used in this study was 27.5%, and considering that most soluble solids in mango composition are mono- and disaccharides (Medlicott and Thompson 1985), the very low T_g of the films is ascribed to the plasticizing effect of these sugars (Ghanbarzadeh and others 2006). Sub-zero T_g values, on the one hand, suggest a relatively poor chemical stability of the films, because of the high molecular mobility (and consequently high reactivity) of its components. On the other hand, such low T_g values imply a very good flexibility of the films even at refrigeration temperatures, which is an advantage concerning the potential use of the material in food packaging applications. Although T_g increases have been small with CNF incorporation, it was significant (Table 1). Some other authors (Psomiadou and others 1996; Anglès and Dufresne 2000; Borges and others 2001; Petersson and Oksman 2006; Alemdar and Sain 2008) reported increases in T_g of biopolymer films by addition of cellulose nanofibers. The increased T_g with CNF incorporation may be ascribed to one or more of the following CNF effects: (1) cellulose–water interactions involve a redistribution of water molecules within the matrix, decreasing the plasticization effect of water (Anglès and Dufresne 2000; Roohani and others 2008; Song and Zheng 2009); (2) interactions between the matrix components and CNF result in a decrease in mobility of the matrix (Lu and others 2005; Song and Zheng 2009); (3) CNF themselves promote an increased crystallinity (and consequently a restricted mobility) of the matrix (Mathew and Dufresne 2002; Azizi Samir and others 2004).

Conclusions

The cellulose reinforcement was well dispersed into the mango puree matrix. The performance of mango puree edible films was noticeably improved by CNF reinforcement. Mechanical properties, except elongation, were improved by the addition of cellulose nanofibers to mango puree edible films. The elastic modulus was the most drastically affected property. Elongation was not impaired at CNF concentrations up to 10 g/100 g. The water vapor permeability was significantly decreased when CNF was incorporated at loadings of at least 10 g/100g. The effect of the filler on glass transition temperature was low but significant.

Acknowledgments

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